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Interactive comment on "Seasonal hydrology drives rapid shifts in the flux and composition of dissolved and particulate organic carbon and mercury in the Fraser River, Canada" *by* B. M. Voss et al.

Anonymous Referee #1

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General Comments: The research presented in this paper represents a substantial new comprehensive data set with relatively high frequency (daily) organic carbon quantity (both dissolved and particulate) measurements as well as quantification of water isotopes, nutrients and dissolved major elements over a dynamic freshet period on the Fraser River. Additionally, the study incorporates in-situ sensor data (FDOM and turbidity) as well as a small mercury data set (6 samples). While this type of data has been collected in other systems, the Fraser River is unique due to its large size and contributions to the coastal environment in Canada and due to its relatively pristine sta-

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tus and non-typical hydrology as a result of local climate and geography which give it an 'elongated' freshet period. Quantifying and understanding carbon dynamics (quantity, quality, and ability of in situ sensors to document changes in these parameters) in such a large and unique system is an important contribution to the regional scientific community. While the overall quality of the data collection effort, compilation of information and analyses are sound, I feel the flow of the paper and presentation of results and discussion can be significantly improved. Regarding the clarity and flow of the paper, in most cases, there is a simple solution; for example, it would be useful to have a single section describing the general watershed characteristics and what makes the system important/unique, as is that information is interspersed throughout the paper. I have listed numerous other instances where re-organization will significantly improve the flow and clarity of the paper within the technical corrections. Another way to improve clarity and flow of the paper is to reduce the amount of figures included (12 total, many of which have multiple images). While I understand the amount of information collected is part of what makes the study unique, much of it is secondary to the main focus of carbon fluxes and patterns during the freshet; many of the graphs could be placed in supplemental material as noted in the technical corrections. Along the same lines, with respect to Hg, while it was useful to sample in conjunction with DOC parameters during this dynamic period, and the preliminary analysis of the dataset is thorough, I would caution any broad conclusions about Hg dynamics and variability with so few samples. While the point is made within the discussion that the data set is limited, I do not think the preliminary findings warrant such a large amount of the discussion as well as inclusion of 'mercury' in the title. In general, this is a very useful study with a thorough discussion which just needs modifications in composition and order.

Technical corrections: In general, the paper could benefit from re-organization, some material in the introduction should be in discussion, some materials in methods would better fit in results, and some in results belong in discussion, as noted below.

Basic watershed/river descriptions are introduced throughout the paper, within the in-

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troduction (p. 7617, l. 20-28 describes the unique hydrology and p. 7618, l. 11-15 describes land use as it may relate to Hg sources), in the discussion (p. 7629-7630 describes 4 specific reasons why the system is unique) and in the conclusions (p. 7641, l. 18-25 describing the general system as pristine and free-flowing); all of this information would be easier to follow presented together and then referenced when necessary within the discussion. In addition, there is no basic information on watershed size and flow contributions to the coast relative to other basins.

Abstract What makes this study unique is the combination of the large data collection effort in conjunction with the unique system under investigation; the change in DOC quantity and quality with flow regime and source areas has been explored in many other studies, but how this large, relatively undisturbed system with unique hydrology compares to other systems and why it is different or similar should be the focus of the interpretation. It is presented in the discussion and conclusions and should be highlighted in the abstract.

Introduction (p. 7615, l. 25-29) The two sentences describing the DOC/POC ratio from prior research don't seem to follow from the rest of the paragraph describing DOC quantity and composition. It is interesting that the ratio is different than other studies, but this information should appear in the discussion along with an evaluation of the current study results, does this ratio still hold? Or did the infrequent data collection (twice monthly) misinform the initial conclusions?

Methods (p. 7622, l. 10-15) The relationship between filtered FDOM and DOC measurements as well as a comparison of the in situ and ex situ FDOM measurements belong within the results/discussion not the methods section. Likely would be better placed in supplemental material.

Methods (p. 7624, l. 2-23) The results for Hg analysis with respect to the detection limit belong in the results, not the methods section.

Results (p. 7625, l. 25-26 through p. 7626, l. 1-10) The description of DOM properties

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and UV metrics belongs in the introduction or methods, not results.

Results (p. 7627, l. 4-8) The explanation of the negative exponential relationship between SPM and POC observed in rivers globally and findings in those studies belong in the discussion section, not the results.

Methods A summary of the time period over which daily samples were taken and for what parameters as well as the time period of in situ measurements needs to be clearly stated at the beginning of the methods. I believe they were all taken at the same time period (though suspended sediment concentration and Hg for only a subset of samples) but this is confusing because the turbidity and organic matter sections are separate from the sample collection section leading the reader to think they were obtained at a different frequency. In many studies in situ instruments (turbidity and FDOM) are deployed over a certain time period at high frequency, but it appears in this study they were used as a one time point measurement to be used in comparison to grab samples. This needs to be stated more clearly in the methods. Perhaps separating field sampling from laboratory methods would be a useful.

Results There is no presentation of the nutrient and dissolved major element data with the exception of noting "modest changes" in those parameters within the first few lines of the discussion. This data should be summarized in the 'water quality trends' section of the results, not just reported in the table. Would one expect the composition to change with carbon dynamics, why or why not?

Discussion: (p 7630, l. 13-16) The DOC yield of the Fraser River is compared to two other nearby rivers, can you speculate on why they would be similar (Yukon) or different (Columbia)? Does it relate to land use/hydrology/climate?

(p.7631m l. 19-21) The sentence compares the fall and spring DOC mobilization quantities, was this information presented in the results?

(p.7639, l.23-24) The range of Hg exported with respect to deposition is stated as 24-47

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percent, which is relatively high compared to results published in more recent studies (see Brigham et al., 2009).

One important purpose of the large data collection mentioned in the introduction was not addressed in the discussion; based on the data findings, what do the authors think the implications will be for a future shift to a more rain-dominated precipitation and earlier freshet that they mention in the introduction?

Figures: While all the figures are useful, they are not all necessary and several could be moved to supplementary information, specifically, figures 2, 4, 5, and 12.

Other relevant citations on Hg and carbon dynamics listed below. Though I recommended this section of the paper be shortened, I think it useful for the authors to be aware of the following papers with respect to Hg and DOC dynamics.

Burns, D.A., Aiken, G.R., Bradley, P.M., Journey, C.A. and Schelker, J. (2013) Specific ultra-violet absorbance as an indicator of mercury sources in an Adirondack River basin. Biogeochemistry. 113:451-466

Demers, J. D., C. T. Driscoll, and J. B. Shanley (2010), Mercury mobilization and episodic stream acidification during snowmelt: Role of hydrologic flow paths, source areas, and supply of dissolved organic carbon, Water Resour. Res., 46, W01511, doi:10.1029/2008WR007021.

Oswald, C. J., and B. A. Branfireun (2014), Antecedent moisture conditions control mercury and dissolved organic carbon concentration dynamics in a boreal headwater catchment, Water Resources Research, 50, 6610–6627, doi:10.1002/2013WR014736.

Riscassi, A.L. and T.M. Scanlon, (2011) Controls on stream water dissolved mercury in three mid-Appalachian forested headwater catchments, Water Resources Research, 47, W12512, doi:10.1029/2011WR010977.

Shanley, J. B., P. F. Schuster, M. M. Reddy, H. E. Taylor, and G. R. Aiken (2002),

Mercury on the move during snowmelt in Vermont, Eos Trans. AGU, 83, 45–48.

Shanley, J. B., N. C. Kamman, T. A. Clair, and A. T. Chalmers (2005), Physical controls on total and methylmercury concentrations in streams and lakes of the northeastern USA, Ecotoxicology, 14(1–2), 125–134.

Shanley, J. B., et al. (2008), Comparison of total mercury and methylmercury cycling at five sites using the small catchment approach, Environmental Pollution, 154, 143–154.

Schuster, P. F., J. B. Shanley, M. Marvin-Dipasquale, M. M. Reddy, G. R. Aiken, D. A. Roth, H. E. Taylor, D. P. Krabbenhoft, and J. F. DeWild (2008), Mercury and organic carbon dynamics during runoff episodes from a northeastern USA watershed, Water Air and Soil Pollution, 187(1–4), 89–108.

Specific comments

Methods Define spectral slope.

Tables and Figures

Table 1. Is there a reason why the units for nutrients and major elements are within the heading and not within the table like all other parameters, there appears to be plenty of room?

Table 2. Second sentence, “Sampling in 2012 was not sufficiently high frequency”, add the word ‘at’

Table 2. Define spectral parameters

Table 3. Note the difference in sample frequency of two different study periods.

Table 4. The definition of ‘fraction’ is not clear

Figure 2. Unsure of what is meant by ‘daily fluctuations in water temperature creating diurnal discharge pulses’, is that from daytime snow melt? Write that explicitly. Some rivers experience daily fluctuations in discharge from evapotranspiration or variations

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in industrial discharges so please clarify.

Figure 2. All other figures focused on freshet period start on March 25, while this image begins on March 18, is there a reason? If not, best to be consistent.

Figure 3. Define 'SPM'.

Figures (3,6,8,9). The figure caption needs some kind of overall description of what is shown, the 'take home message' is useful but secondary.

Figure 3B. What are the 'two measurements' being referred to in the caption used to calculate the SPM concentration difference? Is it the measured SPM and predicted with the turbidity rating? It is unclear as written.

Figure 4. Why not report the r2 for figure 4A, similar to figure 4B?

Figure 5. In the context of the 4-yr period of record, it states 'the change observed during the 1-month freshet is very rapid', but looking at the 4-yr period, it looks like a rapid change occurs each year during this period, though it is not captured in detail due to the infrequent sampling.

Figure 8. 'A' and 'B' should be placed in front of description, not after. Why change from the month label to Julian Day? It would be easier to compare to other graphs if months were used.

Figure 12. Include correlation coefficients since they are referenced.

Interactive comment on Biogeosciences Discuss., 12, 7613, 2015.